

## Chapter 1

# Introduction, definition, and classification of nutrients<sup>☆</sup>

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### Summary

This chapter provides a brief overview of the history of plant nutrition. It is currently accepted that plants require 14 essential mineral elements (nutrients), without which they cannot complete their life cycle. The macronutrients nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg) are required in much larger amounts than the micronutrients iron (Fe), manganese (Mn), boron (B), zinc (Zn), copper (Cu), molybdenum (Mo), nickel (Ni), and chlorine (Cl). Plants also take up beneficial elements, such as sodium (Na), silicon (Si), cobalt (Co), iodine (I), selenium (Se), and aluminum (Al), which can improve resistance to pests, diseases, and abiotic stresses as well as plant growth and crop quality. A scheme to classify plant nutrients according to their biochemical properties and physiological function is presented. A proposal that the current definition of essential nutrients is too narrow to encompass a vision for the future of research in plant nutrition aimed at improving crop production and quality, agronomic practice, and fertilizer use and regulation is discussed. Plant nutrient requirements, and mineral composition, can vary greatly as a consequence of genetic and environmental influences. Extreme variation from the average leaf mineral composition (standard leaf ionome) occurs among some orders of plants: Poales (grasses) are low in Ca, Caryophyllales are high in Mg, and Brassicales are high in S even when sampled from diverse environments. The evolution of such traits has been traced using phylogenetic relationships among angiosperm orders, families, and genera. Variation in the leaf ionome has profound consequences for ecology, mineral cycling in the environment, sustainable agriculture, and livestock and human nutrition.

### 1.1 General

The beneficial effect of adding mineral elements (e.g., plant ash or lime) to soils to improve plant growth has been known in agriculture for more than 2000 years. Nevertheless, even 200 years ago, it was still a matter of scientific controversy as to whether mineral elements functioned as nutrients in plant growth. The first convincing evidence of the important roles they played came from the work of Carl Sprengel (1787–1859) who was both a chemist and an agronomist teaching at the University of Göttingen, Germany. Following extensive chemical analysis of soils and crops, he concluded that 20 elements [including nitrogen (N), phosphorus (P), potassium (K), sulfur (S), magnesium (Mg), and calcium (Ca)] were required for plant growth. It was he, also, who originally postulated the Law of the Minimum, that growth should be restricted by whichever nutrient resource was in most limiting supply. He published this work in 1831 in the first of his two books on agricultural chemistry, but his valuable contribution to plant nutrition remained largely forgotten until relatively recent times. It was the publication of the book of his fellow countryman, the organic chemist, Justus von Liebig (1803–73), *Chemistry and Its Application to Agriculture and Physiology*, in 1840—a best seller, written in both English and German and reprinted and re-edited many times—that highlighted the importance of the mineral nutrition of plants. Unfortunately, the work of Sprengel, although included in von Liebig's book, was not given due acknowledgment despite Sprengel's protestations. Now, almost 200 years later, the contributions of both pioneering scientists are well recognized. Carl Sprengel is considered the true founder of the doctrine of mineral nutrition of plants

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and Justus von Liebig the indefatigable advocate for its acceptance. For a detailed account of the origin and theory of the mineral nutrition of plants see [van der Ploeg et al. \(1999\)](#).

The publication of von Liebig's timely book stimulated an enormous interest in the application of mineral nutrients to soils to increase crop yields. In England, beginning in 1843, John Bennet Lawes (1814–1900) and Joseph Henry Gilbert (1817–1901) set up experimental plots treated with varying amounts of what were then described as mineral manures at Rothamsted Manor in Harpenden ([Dyke, 1993](#)). One of these manures was monocalcium phosphate [ $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ], a soluble phosphate fertilizer produced by treating bones or mineral phosphates with sulfuric acid. This process was patented by Lawes in 1842, who named the product “superphosphate” and sold it from his fertilizer factory founded in 1843. Other manures included muriate of potash (KCl), sulfate of soda ( $\text{Na}_2\text{SO}_4$ ), and sulfate of magnesia ( $\text{MgSO}_4$ ). Nitrogen was supplied as sulfate of ammonia ( $(\text{NH}_4)_2\text{SO}_4$  or nitrate of soda ( $\text{NaNO}_3$ ). Farmyard manure was also applied to the plots. Lawes was very much aware of the importance of N and P for plant growth from his pot experiments testing ammonium phosphate prior to 1840; the benefit of superphosphate in increasing the yields of turnips (*Brassica rapa* subsp. *rapa*) was reported later from the results of the Barnfield plots sown in 1843.

The long-continuing and well-known controversy between Lawes and Gilbert with von Liebig as to how plants obtain N is reviewed in detail by [Dyke \(1993\)](#). In brief, von Liebig, who had little first-hand experience of agronomy, proposed, in the second edition of his book, that plants obtained their N from the atmosphere, whereas Lawes and Gilbert maintained that the soil, and the N fertilizer added to it, constituted the predominant source of N for crops. Results of the Broadbalk winter wheat (*Triticum aestivum*) experiment, sown in 1843, and later findings from the same plots, clearly demonstrated the enormous benefit of applying N fertilizer both in improving the appearance of crops during growth and increasing their yields. Sadly, even when presented with these results, von Liebig flatly refused to admit that he was wrong. To quote [Dyke \(1993\)](#), “If only Liebig had had the grace and humility to admit that, in view of the facts presented by Lawes and Gilbert, he had changed his mind, his reputation with contemporary and later generations of scientists and farmers would have been greatly enhanced.”

## 1.2 Essential elements for plant growth

As evident from the work on field experiments at Rothamsted, the “mineral element theory” as propagated in von Liebig's book went largely untested and the conclusion that mineral elements were required for plant growth was reached mainly by observation and speculation rather than by precise experimentation. This was one of the main reasons for the large number of carefully controlled, experimental studies using solution culture undertaken from the 1840s onwards, and particularly by Wilhelm Knop (1817–1891) and Julius von Sachs (1832–1897) in the 1850s and 1860s. In these experiments plants were deprived of specific elements, and the consequences for growth and development were investigated. Such studies made possible a more precise characterization of nutrient elements and helped determine their role in plant physiology and metabolism. In his book of 1865 on experimental plant physiology, von Sachs identified “essential” and “nonessential” elements. The essential elements included those required for the structure and existence of cells [carbon (C), oxygen (O), hydrogen (H), N, and S] as well as those needed physiologically to maintain growth and the vegetative cycle [K, Ca, Mg, P, and iron (Fe)]. However, it was not until the twentieth century that the requirement of plants for additional elements, present in much smaller amounts in plant tissues, was discovered. Of the 14 mineral nutrients now known to be required for plant growth, two distinct groups are recognized: the macronutrients, N, K, P, S, Ca, and Mg, which are required in large amounts, and the micronutrients Fe, manganese (Mn), boron (B), zinc (Zn), copper (Cu), molybdenum (Mo), nickel (Ni), and chlorine (Cl), which are of equal importance, but required in very much smaller amounts.

[Arnon and Stout \(1939a\)](#) proposed that an element can only be considered essential if the following three criteria are met:

1. a deficiency of it makes it impossible for the plant to complete the vegetative or reproductive stage of its life cycle;
2. such deficiency is specific to the element in question, and can be prevented or corrected only by supplying this element; and
3. the element is directly involved in the nutrition of the plant apart from its possible effects in correcting some unfavorable microbiological or chemical condition of the soil or other culture medium.

These three criteria defining an essential plant nutrient have been more or less universally accepted and appear in numerous publications. However, there are flaws in this proposal, as eloquently summarized by [Epstein \(1999\)](#) and discussed by [Brown et al. \(2022\)](#). Contrary to criterion (1), many plant species may be severely deficient in a nutrient element yet complete their life cycle. Criterion (2) is redundant. Criterion (3) presumes that the designation of an element as essential must entail knowledge of its direct involvement in the nutrition of the plant. This was certainly not the case

for B, which has been known to be essential since Warington (1923) reported that broad bean (*Vicia faba*) and other plant species failed to grow and develop without it, but it was not until 1996 that a definitive role for B in plants was established (Brown et al., 2002).

The essentiality of 14 mineral elements for plants is now well established, although the known requirements for the micronutrients Cl and Ni are, as yet, restricted to a few plant species. Progress in establishing the essentiality of elements has been closely related to developments in analytical chemistry, particularly in the purification of chemicals and the development of new analytical techniques. This relationship is reflected in the time-course of the discovery of the essentiality of the micronutrients (Table 1.1).

### 1.3 Beneficial elements for plant growth

Plants also take up another group of elements that are described as beneficial because they can improve plant growth and crop quality, as well as resistance to pests, diseases, and abiotic stresses. These include sodium (Na), silicon (Si), cobalt (Co), iodine (I), selenium (Se), and aluminum (Al) (for a review of these and other beneficial elements see Barker and Pilbeam, 2015). For several of these elements, whether they should be classified as an essential nutrient or a beneficial element is not clear-cut. For example, Na is required in similar amounts to micronutrients for the C4 photosynthetic pathway (Cheeseman, 2015) and also promotes the growth of euhalophytes, such as beet (*Beta vulgaris*) and saltbush (*Atriplex* spp.), when present in tissues in similar quantities to macronutrients (Debez et al., 2017).

Tissues of many field-grown crops contain Si in similar concentrations ( $1\text{--}100\text{ mg g}^{-1}$  dry weight) to those of the macronutrients (Hodson et al., 2005) and in grass-like monocotyledonous plants, such as rice (*Oryza sativa*) and sugar cane (*Saccharum officinarum*), Si may be the predominant mineral constituent. Silicon, in the form of solid amorphous silica or phytoliths, provides structure and rigidity to aboveground plant parts (Epstein, 1999). Silicon also alleviates deleterious effects caused by abiotic stress (e.g., drought and salinity) and protects plants from biotic stress (e.g., pests and diseases), as reviewed by Luyckx et al. (2017). Recently, the supply of Si has been shown to influence the uptake and translocation of all the macronutrients and some of the micronutrients (Pavlovic et al., 2021). Application of Si fertilizers has been shown to increase yield and quality of both monocotyledonous and dicotyledonous crops grown in the field (Liang et al., 2015). Even in tomato, a plant that contains much less Si than rice or sugar cane, the application of Si in field trials increased yield by 15%–30% by increasing both fruit number and fruit size (Liang et al., 2015).

Nutrient solutions rarely include Si because it is not considered essential for plant growth. Epstein (1994) contends that the omission of Si from nutrient solutions amounts to the “imposition of an atypical environmental stress.” This statement is supported by the findings of Gottardi et al. (2012) who observed that the addition of only  $30\text{ }\mu\text{M}$  Si to the solution of hydroponically grown corn salad (*Valerianella locusta*) increased edible yield, raised crop quality, and extended shelf life. Similarly, Pozo et al. (2015) demonstrated that the addition of  $0.65\text{ mM}$  Si to the nutrient solution of several hydroponically cultivated horticultural crops [lettuce (*Lactuca sativa*), tomato, sweet pepper (*Capsicum annuum*), melon (*Cucumis melo*), cucumber (*Cucumis sativus*)] not only increased vegetative growth but also increased the thickness of plant cuticles, which protected the crops from fungal infection by *Botrytis cinerea*.

Cobalt (Co), in common with the micronutrients Fe, Mn, Cu, and Zn, is classified as a transition metal in the periodic table. It is required for symbiotic  $\text{N}_2$  fixation in nodulated legumes, where Co is an integral component of cobalamin

**TABLE 1.1** Discovery of the essentiality of micronutrients for plants.

Element (chemical symbol)	Year	Discovered by
Fe	1843	E. Gris
Mn	1922	J.S. McHargue
B	1923	K. Warington
Zn	1926	A.L. Sommer and C.B. Lipman
Cu	1931	C.B. Lipman and G. MacKinney
Mo	1939a,b	D.I. Arnon and P.R. Stout
Cl	1954	T.C. Broyer et al.
Ni	1987	P.H. Brown et al.

(vitamin B<sub>12</sub>) which is required by several enzymes involved in N<sub>2</sub> fixation by rhizobial bacteria. Cobalt is also essential for N<sub>2</sub> fixation by endotrophic and associated bacteria in plant roots, which can contribute substantially to N acquisition by various crops (Reed et al., 2011). Symptoms of Co deficiency (similar in appearance to those of N deficiency) have been reported in both legume and nonlegume plant species, and it seems likely that coenzymes or proteins containing Co participate in plant Co metabolism. The possibility that Co is an essential nutrient for plants was reviewed recently by Hu et al. (2021).

A case for including I among the essential nutrients for plants was presented by Kiferle et al. (2021), who reported impaired growth of arabidopsis (*Arabidopsis thaliana*) plants lacking I and the presence of iodinated proteins in shoots and roots that might function in photosynthetic processes and antioxidant activities, respectively.

## 1.4 A new definition of a mineral plant nutrient

It has been argued that the current distinction between an *essential nutrient* and a *beneficial element* for plant growth does not support a future vision for plant nutrition that encompasses plant science research, practical agronomy, and fertilizer legislation. Brown et al. (2022) propose that a mineral plant nutrient might be defined more broadly as “an element which is essential or beneficial for plant growth and development or for the quality attributes of the harvested product of a given plant species grown in its natural or cultivated environment”. The authors suggest that this new, broad definition, founded in science and relevant in practice, has the potential to revitalize innovation and discovery in plant nutrition. Furthermore, this new definition would align better with nutrients deemed essential for animal and human nutrition (White and Broadley, 2009). The new definition represents a fundamental change in concept, but, nevertheless, it is in keeping with the practical, historic objectives of plant nutrition to improve fertilizer usage and crop production. Brown et al. (2022) see the new concept of a plant nutrient as a starting point for open debate and discussion. They also envisage that an independent global scientific body, such as, for example, the International Plant Nutrition Council, would review the list of essential and beneficial elements periodically in the light of new scientific findings. The inclusion of both essential and beneficial elements in the proposed definition of a plant nutrient is important because in many current legislative jurisdictions “beneficial element” is interpreted as “not a plant nutrient”. This does not serve agriculture well and is in urgent need of revision. It is of particular relevance to Si in view of the overwhelming evidence of the importance of Si for crop yield and quality (Liang et al., 2015).

## 1.5 Biochemical properties and physiological functions of nutrient elements in plants

In addition to their relative concentrations within the plant, elements may also be classified broadly according to their biochemical properties and physiological function. In a scheme proposed by Mengel and Kirkby (2001), all plant nutrients including carbon (C), hydrogen (H), and oxygen (O) as well as two beneficial elements (Na and Si) were classified into four groups (Table 1.2).

The first group incorporates the major constituents of organic plant material: C, H, O, N, and S. These elements are constituents of amino acids, proteins, enzymes, and nucleic acids, the building blocks of life. The assimilation of all these nutrients by plants is closely linked with oxidation–reduction reactions.

Phosphorus, B, and Si constitute a second group of elements. All three occur in the form of inorganic anions or acids in plants or are bound by hydroxyl groups of sugars to form phosphate, borate, and silicate esters. Phosphorus is a key component of the nucleic acids DNA and RNA, as well as membrane phospholipids. Boron is essential for cell wall structure and membrane integrity. Silicon, taken up as silicic acid, is polymerized to solid amorphous hydrated silica, which maintains the structure and rigidity of aboveground parts in many plant species. Silicon also protects plants from a variety of biotic and abiotic stresses (Epstein, 1999).

The third group of elements comprises K, Na, Ca, Mg, Mn, and Cl, all of which are taken up from the soil solution in their ionic forms. Within the plant these ions have non-specific functions, for example, in establishing electrochemical gradients across plant membranes, in maintaining cation–anion balance within cell compartments, and in long-distance nutrient transport. In addition, K activates numerous enzymes, is required for protein synthesis, and is closely involved in photosynthesis at various levels. Potassium fluxes determine stomatal aperture and, thereby, transpiration and C assimilation. Calcium binds strongly to carboxyl groups of pectins in cell walls, plays a fundamental role in membrane integrity, and acts as a second messenger in the form of cytosolic free Ca<sup>2+</sup> in many developmental and physiological processes (White, 2015). Magnesium, like K, activates numerous enzymes. The biochemistry of adenosine triphosphate, which is central to energy metabolism in plant cells, has an absolute requirement for Mg. Magnesium also

**TABLE 1.2** Classification of plant nutrients.

Nutrients	Uptake	Biochemical functions
<i>Group 1</i>		
C, H, O, N, S	as CO <sub>2</sub> , HCO <sub>3</sub> <sup>−</sup> , H <sub>2</sub> O, O <sub>2</sub> , NO <sub>3</sub> <sup>−</sup> , NH <sub>4</sub> <sup>+</sup> , N <sub>2</sub> , SO <sub>4</sub> <sup>2−</sup> , SO <sub>2</sub> ions from the soil solution, gases from the atmosphere	<ul style="list-style-type: none"> <li>• Major constituents of organic material.</li> <li>• Essential elements of cofactors and enzymes.</li> <li>• Assimilation by oxidation–reduction reactions.</li> </ul>
<i>Group 2</i>		
P, B, Si	as phosphates, boric acid, and silicic acid from the soil solution	<ul style="list-style-type: none"> <li>• Esterification with alcohol groups</li> <li>• Phosphate esters involved in energy transfer reactions and phospholipids.</li> </ul>
<i>Group 3</i>		
K, Na, Ca, Mg, Mn, Cl	as ions from the soil solution	<ul style="list-style-type: none"> <li>• Non-specific functions in establishing osmotic potential.</li> <li>• More specific functions for optimal conformation of enzymes (enzyme activation).</li> <li>• Bridging of reaction partners.</li> <li>• Charge balance.</li> <li>• Controlling membrane permeability and electrochemical potential.</li> </ul>
<i>Group 4</i>		
Fe, Cu, Zn, Mo, Ni	as ions or chelates from the soil solution	<ul style="list-style-type: none"> <li>• In chelated form in prosthetic groups of enzymes.</li> <li>• Enable electron transport by valency change.</li> </ul>
Source: From Mengel and Kirkby (2001).		

functions in protein synthesis. Magnesium can be bound strongly by coordinate and covalent bonds, by so-called chelation, as occurs in the chlorophyll molecule, which allows plants to absorb energy from light in photosynthesis.

The capacity of Mg, Ca, and Mn to form chelates means that these elements resemble those of the fourth group of elements (Fe, Cu, Zn, Ni, and Mo). The latter micronutrients also have specific functions: iron in the synthesis of chlorophyll, Cu in proteins in photosynthesis, respiration and lignification, and Cu, Zn, and Mn in superoxide dismutase isoenzymes that eliminate toxic O<sub>2</sub><sup>−</sup> radicals. Additionally, Zn plays a role in membrane integrity, protein synthesis, and the synthesis of the phytohormone indole-3-acetic acid. Molybdenum is a component of nitrate reductase and the nitrogenase required for N<sub>2</sub> fixation (Kopsell et al., 2015). Nickel is a component of urease and hydrogenase. Treatment of soybean seeds with Ni improves biological N<sub>2</sub> fixation and urease activity (Lavres et al., 2016). Cobalt is required for rhizobial N<sub>2</sub> fixation in nodulated legumes.

Critical leaf concentrations of macro- and micronutrients, as well as the functions of these nutrients and their mobility within plants have been reviewed by Grusak et al. (2016). Leaf macronutrient concentrations considered adequate for maximal plant growth are in the range of (mg g<sup>−1</sup> dry weight): N (15–40), K (5–40), P (2–5), S (1–5), Ca (0.5–10), and Mg (1.5–3.5). Leaf micronutrient concentrations considered adequate for plant growth are in the range of (μg g<sup>−1</sup> dry weight): Cl (100–6000), B (5–100), Fe (50–150), Mn (10–20), Cu (1–5), Zn (15–30), Ni (≈ 0.1), and Mo (0.1–1.0). The average concentrations of mineral elements are given in Table 1.3. Detailed accounts of the biochemistry and physiology of macronutrients, micronutrients, and beneficial elements are presented in Chapters 6, 7, and 8, respectively.

## 1.6 Variation in the angiosperm ionome

The ionome is defined as the mineral elemental composition of a subcellular structure, cell, tissue, organ, or organism; it is strongly influenced by interactions between genetics and the environment (Neugebauer et al., 2018). White et al. (2012) confirmed the robustness of shoot ionomes from seven families with 21 plant species growing on six plots of the Rothamsted Park Grass Continuous Hay Experiment, supplied with different fertilizer treatments since 1856 (Dyke, 1993). Regardless of these continuous long-term treatments, plant families could be distinguished by their shoot

**TABLE 1.3** Average concentrations of mineral elements in shoot dry matter (d. wt) sufficient for adequate growth.

Element	Chemical symbol	mmol kg <sup>-1</sup> d. wt	mg kg <sup>-1</sup> d. wt
Molybdenum	Mo	0.001	0.1
Nickel <sup>a</sup>	Ni	0.001	0.1
Copper	Cu	0.1	6
Zinc	Zn	0.3	20
Manganese	Mn	1.0	50
Iron	Fe	2.0	100
Boron	B	2.0	20
Chlorine	Cl	3.0	100
Sulfur	S	30	1000
Phosphorus	P	60	2000
Magnesium	Mg	80	2000
Calcium	Ca	125	5000
Potassium	K	250	10,000
Nitrogen	N	1000	15,000

<sup>a</sup>Based on *Epstein and Bloom (2005)* and *Brown et al. (1987)*.

ionomes. The most informative elements for discriminant analysis followed the sequence Ca > Mg > Ni > S > Na > Zn > K > Cu > Fe > Mn > P.

The “standard functional ionome” comprises the concentrations of the 14 mineral nutrients in tissues of the “average” angiosperm when growth is not limited by mineral nutrition. Variations from the standard ionome can be used to compare the effects of genetics and environment on the ionome. The environment exerts a significant influence on the leaf ionome by affecting growth and development as well as the phytoavailability of mineral nutrients in the soil. Particular orders of plant species show specific leaf ionic characteristics even when sampled from diverse environments. Leaves of Poales (grasses) are relatively low in Ca, whereas those of Caryophyllales [e.g., quinoa (*Chenopodium quinoa*), sugar beet (*Beta vulgaris*)] are high in Mg, and Brassicales [e.g., cabbage (*Brassica oleracea*), oilseed rape (*Brassica napus*)] are high in S. The evolution of ionic traits have been traced using phylogenetic relationships among angiosperm orders, families, and genera. Consequences of variation in the leaf ionome for ecology, mineral cycling in the environment, sustainable agriculture, and livestock and human nutrition have been discussed by *Neugebauer et al. (2018)*.

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